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# Standard for Storing and Using Peroxidizable Organic Chemicals

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Lawrence Livermore National Laboratory

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# Preface

This publication provides practical direction to people who use peroxidizable chemicals in a chemistry laboratory setting and in other settings.

The authors wish to express their sincere thanks to Ruth Hawley-Fedder for her thoughtful comments offered as peer reviewer for this document.

**Lawrence Livermore National Laboratory**

# Storing Peroxidizable Chemicals

## 1.0 Purpose

This document is intended to assure that susceptible materials are stored and used in a manner that will minimize unintended peroxidation and prevent fires and explosions that can result from the use of peroxidized solvents by

- Providing direction for storing and using peroxidizable organic chemicals.
- Specifying means to slow the formation of peroxides, detect peroxides, record the results of periodic testing, and treat or dispose of peroxidized materials.

This document describes the requirements that are most important for day-to-day operations and is based on "Review of Safety Guidelines for Peroxidizable Organic Chemicals," a paper, published in a peer-reviewed journal, that provides guidance for handling peroxidizable chemicals.

## 2.0 Reference

R. J. Kelly, "Review of Safety Guidelines for Peroxidizable Organic Chemicals," *Chemical Health & Safety*, September/October 1996, pp 28–36.

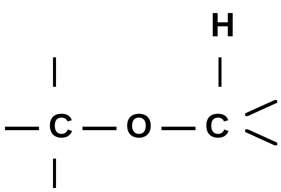
This paper is available within Lawrence Livermore National Laboratory (LLNL) by calling one of the four area Environment, Safety, and Health (ES&H) Teams, which provide the local Occupational Safety and Health (OSH) service throughout the Laboratory. In cases where this document does not provide specific guidance, the user should consult the local OSH service. The user may also use guidance provided by the vendor and available in scientific literature.

## 3.0 Description of Affected Materials

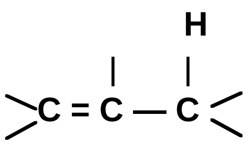
A wide variety of organic compounds spontaneously form peroxides by a free-radical reaction with molecular oxygen in a process of auto-oxidation. Although ethers are the most notorious in this regard, many other moieties are susceptible to the same process (see Table 1, where these moieties are numbered 1 to 14 from most to least likely to form organic peroxides).

**Table 1. Moieties that can form organic peroxides.**

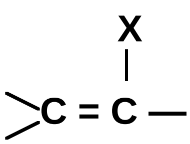
1. Ethers and acetals with α-hydrogen



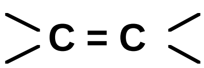
2. Alkenes with alylic hydrogen



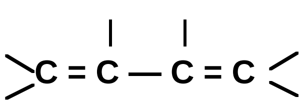
3. Chloroalkenes, fluoroalkenes



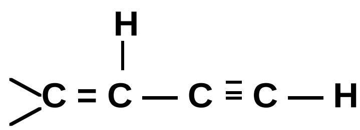
4. Vinyl halides, esters, ethers



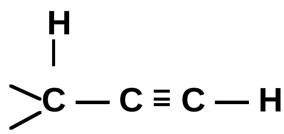
5. Dienes



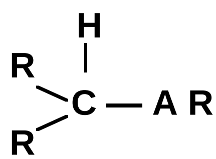
6. Vinylalkynes with α-hydrogen



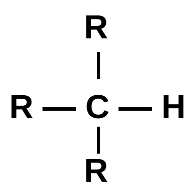
7. Alkylalkynes with α-hydrogen



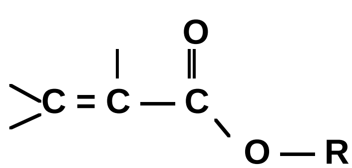
8. Alkylalkynes with tertiary α-hydrogen



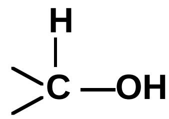
9. Alkanes and cycloalkanes with tertiary hydrogen



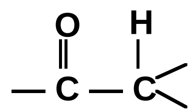
10. Acrylates, methacrylates



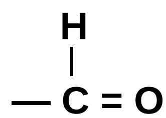
11. Secondary alcohols



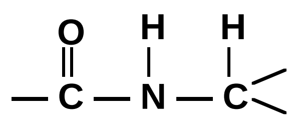
12. Ketones with α-hydrogen



13. Aldehydes



14. Ureas, amides, and lactams with α-hydrogen atom on a carbon attached to nitrogen



Recommended storage limits and more specific guidance for common chemicals that can form peroxides are listed in Table 2. The storage time limits in Table 2 are provided as the basis for policy. This table is organized as follows:

- **Chemicals that form potentially explosive peroxides without concentration:** The first column lists materials that may spontaneously form peroxides that will make the material shock- or heat-sensitive "on the shelf," that is, without any further concentration through evaporation or distillation.
- **Chemicals that form potentially explosive peroxides when concentrated:** The second column lists chemicals that form peroxide levels that make the parent container shock sensitive only when the parent liquid is evaporated, which effectively concentrates the peroxides. This class of peroxidized chemicals has a propensity for exploding when used experimentally in operations such as distillations. Very volatile materials in Column 2, such as diethyl ether, may evaporate if stored without a cap, and the resulting concentrated, peroxidized material may be shock sensitive.
- **Chemicals that autopolymerize:** The third column lists chemicals that may autopolymerize (and thus explode) when relatively small quantities of peroxides are formed.

If chemicals are stored or used in a manner that promotes peroxidation (i.e., exposed to light, heat, or air), a shorter storage limit may be appropriate. Examples of such operations might include closed-circuit spraying of a peroxidizable solvent in air or use of a peroxidizable solvent in a dip or cleaning tank. In these cases, operation-specific storage and use limits should be developed based on empirical testing of the solvent for peroxide accumulation.

Table 2. Common chemicals that form explosive levels of peroxides and their storage limits.[a,b]

| Form potentially explosive peroxides without concentration (3-month storage)[c] | Form potentially explosive peroxides on concentration[d,e] (12-month storage) | Autopolymerize (24-hour to 12-month storage)[f] |
|---|---|---|
| Butadiene[g] | Acetal | Acrylic acid |
| Chloroprene[h] | Acetaldehyde | Acrylonitrile |
| Divinyl acetylene | Benzyl alcohol | Butadiene[i] |
| Isopropyl ether | 2-Butanol | Chloroprene |
| Tetrafluoroethylene[g] | Cyclohexanol | Chlorotrifluoroethylene |
| Vinylidene chloride | 2-Cyclohexen-1-ol | Methyl methacrylate |
| | Cumene | Styrene |
| | Decahydronaphthalene | Tetrafluoroethylene |
| | Diacetylene | Vinyl acetate |
| | Dicyclopentadiene | Vinyl acetylene |
| | Diethyl ether | Vinyl chloride |
| | Diethylene glycol dimethyl ether | Vinyl pyridine |
| | Dioxanes | |
| | Ethylene glycol dimethyl ether | |
| | 4-Heptanol | |
| | Methyl acetylene | |
| | Methyl isobutyl ketone | |
| | 3-Methyl-1 butanol | |
| | Methyl cyclopentane | |
| | 2-Pentanol | |
| | 4-Pentene-1-ol | |
| | 1-Phenylethanol | |
| | 2-Phenylethanol | |
| | 2-Propanol (isopropanol, “IPA”) | |
| | Tetrahydrofuran | |
| | Tetrahydronaphthalene | |
| | Vinyl ethers | |
| | Other secondary alcohols | |

[a] Materials other than those listed may form peroxides. Contact your local OSH service for further information. Applies only to pure materials.

[b] Contact your local OSH service for advice about mixtures.

[c] Store under nitrogen, if practical.

[d] *WARNING! May become unstable if concentrated intentionally or accidentally by the user.*

[e] Test chemicals in Groups 1 through 7 on Table 1 within 12 months of receipt, and discard or deperoxidize if necessary. Test chemicals in Groups 8 through 14 on Table 1 within 12 months of opening, and discard or deperoxidize if necessary.

[f] Chemicals to be stored for ≤5 days if uninhibited or 12 months if inhibited. Avoid storing inhibited materials under inert gas because some inhibitors require a small amount of oxygen to work.

[g] When stored as an inhibited liquid monomer.

[h] When stored as a liquid monomer.

[i] When stored as a gas.

# 4.0 Practices for Control of Peroxidizable Organic Materials

## 4. 1 Inhibitors

Many methods can be used to stabilize or inhibit the peroxidation of susceptible chemicals. If it does not interfere with the use of the chemical and if available, peroxide scavengers (inhibitors) shall be added in small quantities, and peroxidizable chemicals shall be ordered with inhibitor added.

## 4.2 Purchase

Susceptible chemicals should be purchased at planned intervals to ensure that they are used completely before they can become peroxidized.

## 4.3 Storage

Peroxidizables shall be stored in sealed, air-impermeable, light-resistant containers. Diethyl ether should be stored in steel containers because the iron neutralizes peroxides. Consult your local chemical safety procedures and OSH service to see if additional information is available.

Peroxidizable chemicals shall be stored in cool locations. For more information on storage in cool locations or use of refrigerators and freezers, consult your local chemical safety procedures and OSH service.

Peroxidizable chemicals shall be stored and used under an inert atmosphere, when practical.

## 4.4 Labeling and Shelf-Life Limitation

In order to implement a shelf-life limit program for auto-oxidizable chemicals, each container of peroxidizable chemical shall be labeled with the date received by the user and the date opened. The end user is responsible for labeling the containers. Labels are available from the local OSH service. The user shall assign an appropriate expiration date to containers, using Table 2 for guidance. If Table 2 does not provide guidance about a specific chemical, then information from the chemical vendor or scientific literature may be used for guidance.

WARNING: MAY FORM EXPLOSIVE PEROXIDES

**Store in tightly closed original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, contact your ES&H Team immediately. Check for peroxides before distilling or concentrating.**

THIS CHEMICAL HAS A LIMITED SHELF LIFE

**Container received on: ____________________________________**

**Container opened on: _____________________________________**

**Test or dispose of ________ months after receipt**

**or _______ months after opening.**

TESTING, DEPEROXIDATION,
AND STABILIZATION RECORD

**Test Date____ Peroxides______ Post-treatment_____ Inhibitor Added _____**

**Test Date____ Peroxides______ Post-treatment_____ Inhibitor Added _____**

**Test Date____ Peroxides______ Post-treatment_____ Inhibitor Added _____**

**Figure 1. LLNL Peroxide-forming chemicals label.**

## 4.5 Testing and Deperoxidation

When the date on the container expires, the peroxide-forming chemical shall either be (1) tested for peroxide content or (2) assumed to contain excessive peroxides and disposed of as hazardous waste. The maximum allowable concentration of peroxide in chemicals is 100 parts per million (ppm). If a value over 100 ppm of peroxide is detected, the owner shall deperoxidize the chemical or dispose of it as hazardous waste. If the user decides to deperoxidize the material, the most suitable deperoxidation method for the material's intended use shall be selected. Organizations planning to test and deperoxidize materials shall check the reference for guidance about the potential hazards of and procedures used for testing and deperoxidation. If the chemcial is deperoxidized, new dates should be put on the label. The "container opened on" date should be the date the chemical was deperoxidized.

Because of the hazards inherent in some peroxidation methods, testing and deperoxidation shall be carried out using procedures developed in accordance with applicable OSH management practices.

**WARNING:** Contact the Fire Department immediately (dial 911) if there is reason to believe that dangerous levels of peroxides may be present in a container. Also contact your ES&H Team.

### 4.6 Use of Peroxidizables for Purposes Other Than Chemistry

LLNL uses many containers of potentially peroxidizable alcohols for non-chemistry and "low-stress" chemistry purposes (e.g., wipe cleaning and solvent extraction). There is no evidence to suggest that peroxidizable alcohols pose a hazard when used in these ways, even if they become peroxidized to concentrations above 100 ppm. Thus, where potentially peroxidizable alcohols are used for purposes that do not involve heating, chemical reaction, bulk evaporation, or other activities that may stress the peroxidized material (e.g., cleaning in optics laboratories, physics laboratories, or workshops or chemical extraction in chemistry laboratories), it is not necessary to track and test the containers for peroxidation. This exemption does not apply if these materials are used for chemical operations such as distillations and synthetic reactions, and containers with these materials should be labeled as shown in Figure 2.

| |
|---|
| **WARNING: MAY FORM PEROXIDES THAT COULD EXPLODE IF HEATED, CONCENTRATED, OR USED IN CHEMICAL REACTIONS.**<br>**Use only for** ***(to be filled in by user)*** **. Test for peroxides before transferring to Chemical Exchange Warehouse (CHEW) or disposing of as hazardous waste. Contact your Health and Safety Technician or Waste Technician for Guidance.**<br><br>**Date Labeled** ***(To Be Filled In By User)*****.** |

**Figure 2. LLNL labeling for low-stress and nonchemistry peroxidizable alcohols.**

**NOTE:** Only essentially anhydrous alcohols are subject to peroxidation. Solutions of alcohols with water (e.g., rubbing alcohol, which is 70% 2-propanol and 30% water) are not subject to peroxidation and do not need to be labeled, tracked, or tested.

## 4.7 Special Operations Involving Peroxidizable Materials

Operations that expose susceptible materials to oxygen, heat, light, or evaporation may be particularly hazardous and shall be individually reviewed in accordance with local OSH management practice.

Consult the local OSH service and follow local OSH management practice for guidance on conducting the following operations:

- Distilling peroxidizable chemicals.
- Using peroxidizable chemicals in open surface (dip) tanks.
- Spraying peroxidizable chemicals.
- Heating or evaporating peroxidizable chemicals.